

SOME ASPECTS OF WEAKLY CONDUCTING, IONIZED GASES *

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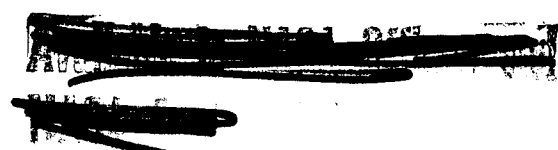
Peter M. Livingston

University of Wisconsin Theoretical Chemistry Institute
Madison, Wisconsin

ABSTRACT

Several complementary aspects of current conduction in multicomponent weakly ionized gases are considered. The first of these is a systematic generalization of the ion current densities in essentially a power series in the ion to neutral concentration ratios derived from multicomponent kinetic theory arguments. The usual definition of ion mobility is shown to be a function of these ratios and lacks uniqueness near the system electrodes if the first order terms are retained. A consequence of this result is that the usual experimental assumption that the ratio of the ion binary diffusion coefficient to its mobility is a function of the system temperature is shown to be valid only in regions of negligible space charge and vanishing ion concentrations. The second result is a numerical study of a simple four-component system showing the development of ion sheaths near the electrodes as a function of both ionization intensity and electron attachment frequency. A plot of the ratio of electron to negative ion current in the external circuit as a function of the latter parameter for fixed ionization intensity suggests a possible determination of the attachment process in oxygen as a function of ionization density.

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Introduction

Simple theories of current transport often suffice as a foundation for the analyses of many experiments in gaseous electronics, and for the interpretation of ion chamber phenomena. However, the systematic extension of the conduction equations to include space charge effects[†] near the electrodes as well as certain other phenomena, requires a more general analysis to include ion concentration dependence and an appropriate generalization of the diffusion coefficients. Generally speaking, the added information obtained from such extended treatments would deal primarily with the ion density profiles occurring near the electrodes. These regions of pronounced charge imbalance, are often referred to as polarization or "sheath" effects, and served to modify current flow in the system more or less profoundly depending on the degree of ionization. Particularly in the case of a Townsend discharge, where ion multiplication occurs in the electrode sheaths, the extent and nature of these regions has an important bearing on the subsequent current and the usefulness of generalized conduction equations is apparent.

It is also true that the local electric field in the inter-electrode space is "shaped" by the nature of chemical reactions affecting the number and mobility of the ions on their course to the electrodes. While it is true that the generalized current expressions are needed as described above, useful semiquantitative

results may be obtained with the usual assumption that the mobilities of the various ions are independent of ion concentrations. A special case of a system of this type will be analyzed in this paper; namely, one with three charged species where the negative ions are formed by attachment of free electrons to the neutral molecules. It happens that the charge conservation feature of this problem considerably simplifies its mathematical structure, but the chief reason for its consideration is that it also represents a technique for the experimental measurement of electron attachment coefficients. As often happens in the latter case, the electron/ion space charge effects are ignored and current flows in response to externally applied fields only. Certainly under the experimental conditions chosen (currents measured in picoamperes) such an assumption is justified. But many applications of electron attachment in more intensely ionized systems demand additional knowledge of the latter coefficient's possible concentration dependence, and therefore the model developed in the latter part of this paper will be of interest.

Generalized Charge Transport

As is well known, the current flow between electrodes in an ionized gas may be treated to a high degree of precision by means of the multicomponent fluid dynamic equations describing conservation of ion species, fluid momentum and energy, and Maxwell's equations for the associated electromagnetic field. Two constitutive equations

are needed to complete the fluid description; an equation of state for the gas and the functional form of the ion current densities. This intractable set of equations can be simplified by a number of approximations. For systems considered "weakly ionized" (ion densities less than 10^{-5} neutral species density), and with average electric fields less than the Townsend threshold, it is often possible to ignore heat and momentum transport, self-generated magnetic fields and chemical reactions among the ions. Time dependent problems sometimes may be further linearized in the electric field and treated analytically.⁽¹⁾ Our present consideration will cover the steady state in the weak ionization limit. In this case the relevant descriptive variables are; the set of all number densities, n_i ; the average component velocities, \bar{v}_i , the scalar pressure, p ; the charge density, ρ ; and the electric field, \underline{E} . The applied voltage, ionization source, and temperature then appear as parameters in the solution to the combined field and continuity equations for the system.

Consider an N component system consisting of a neutral component ("1"), and $N-1$ ionized species contained in a vessel of volume, V , with two electrodes as part of the walls. The gas is maintained at a fixed temperature, T , and the external ionization source uniformly illuminates the gas between the electrodes, maintained at a potential difference, V_0 , by a constant voltage source. The current density for the i -th species is then defined as;

$$\underline{j}_i = n_i e_i \bar{V}_i \quad i = 2, \dots, N \quad (1)$$

where $e_i = \pm Z_i e$ is the charge of the i -th ion, and the total current density is the sum;

$$\underline{j} = \sum_{i=2}^N \underline{j}_i \quad (2)$$

The motion of the gas as a whole is given by the mass average or stream velocity;

$$\underline{v}_0 = \frac{\sum_{i=1}^N m_i n_i \bar{V}_i}{\sum_{i=1}^N m_i n_i} = \bar{v}^{-1} \sum_{i=1}^N m_i n_i \bar{V}_i \quad (3)$$

where \bar{v}^{-1} is the mass weighted specific volume. Finally the total number and charge densities are defined by;

$$n = \sum_{i=1}^N n_i \quad (4)$$

and

$$\rho = \sum_{i=2}^N e_i n_i \quad (5)$$

In the absence of turbulence, the lack of any macroscopic magnetic fields is a necessary and sufficient condition that the mass average velocity be irrotational. Therefore the fluid momentum conservation may be written as:

$$\rho \text{ grad } \frac{1}{2} \underline{v}_0^2 = -\text{grad} p + \rho \underline{E} \quad (6)$$

in the steady state. Except for mass average velocities approaching the local speed of sound in the system, the term in $\text{grad } \frac{1}{2} \underline{v}_0^2$ on the left of the above equation (the so-called "inertial term") may be dropped, as it is very small. Now eq. 6, the species continuity equations, the perfect gas law;

$$p = nkT \quad (7)$$

and a functional form of the current densities, eq. 1, provide a consistent mathematical description in terms of the macroscopic variables previously given.

In most studies, the ion current densities are assumed linear in gradients of the ion concentrations, the pressure and the electric field. This choice can be shown to be valid by the general arguments of irreversible thermodynamics⁽²⁾ or the detailed analysis of the multi-component kinetic theory of gases⁽³⁾, provided the system is not far from equilibrium. After elimination of pressure in favor of the number density and temperature by means of the

equation of state, the above arguments hold that;

$$\underline{d}_i = \text{grad}(n_i/n) + (n_i/n - n_i m_i / \xi) \text{grad} \ln(n) - (n_i m_i / nkT \xi) (e_i \xi / m_i - \rho) \underline{E}$$

$$i=1, \dots, N$$

$$(8)$$

is the driving force acting on a fluid element of the i -th component of the system, where the form has been chosen such that;

$$\sum_{i=1}^N \underline{d}_i = 0$$

$$(9)$$

This constraint follows from the requirement that the motion occurring from eq. 9 be relative to the center of mass of the system. Therefore the driven current densities are linear in the generalized forces;

$$\underline{j}_i = (n^2 e_i / \xi) \sum_{j=1}^N m_j D_{ij} \underline{d}_j + e_i n_i \underline{v}_0 ; \quad i = 2, \dots, N$$

$$(10)$$

and

$$n_1 \underline{v}_1 = (n^2 / \xi) \sum_{j=1}^N m_j D_{1j} \underline{d}_j + n_1 \underline{v}_0$$

$$(11)$$

The coefficients, D_{ij} , in the above equations are referred to as the multicomponent diffusion coefficients and are discussed in detail elsewhere⁽³⁾. From the definition of the mass average velocity and the current densities, it follows that these coefficients are not

all independent, but that;

$$\sum_{i=1}^N m_i D_{ij} = 0 ; j=1, \dots, N \quad (12)$$

In accordance with the reference given above, the independence may be restored to the description provided the choice $D_{ii} = 0$ is arbitrarily made. In the case of a two component system, it follows from the definition of these quantities that they reduce identically to the usual binary diffusion coefficients.

The system of equations given in eqs. 10 and 11 are inadequate to specify the various current densities and the neutral component average velocity uniquely. Additional information must be supplied by integration of one continuity equation for any component or by integration of the continuity equation for the fluid as a whole. Under most circumstances, the electrodes merely discharge ions and accept electrons, and since the system walls are impenetrable, mass is conserved and;

$$\text{div}(\xi \underline{v}_0) = 0 \quad (13)$$

For laminar flow, \underline{v}_0 may be written as the gradient of a scalar, which in turn is harmonic in the volume, V . Therefore, \underline{v}_0 , is a constant in magnitude everywhere. The choice of this constant is established by the following considerations;

- a) all specie velocities are finite throughout the volume,
- b) all charged ion densities are zero at the electrode of the same sign.

Let all the positive ions be labelled with indices k in the range, $(2 \leq k \leq r)$ and all negative ions be similarly labelled with k in the range $(r+1 \leq k \leq N-1)$. If free electrons are present, we shall assign them the index N . All positive ions discharged at the negative plate appear as neutral molecules, therefore;

$$-n_{i-1} \bar{V}_{i-1} = \sum_{k=2}^r n_k \bar{V}_k \alpha_k \quad (14)$$

and likewise at the positive plate;

$$n_{i-1} \bar{V}_{i-1} = - \sum_{k=r+1}^{N-1} n_k \bar{V}_k \quad (15)$$

where α_k, β_k are stoichiometric coefficients (i.e., $2O \rightarrow O_2 + 2e$, $\alpha = 2$) which are hereafter taken as 1 without qualitatively affecting the arguments. The mass of the positive ions is $m_k = (m_1 - Z_k m_e)$, and that of the negative ions is $(m_1 + Z_k m_e)$, where the index k belongs in the range appropriate to either the negative or positive ions. Hence at the electrodes, we find that the (constant) mass flux is;

$$\frac{1}{\rho} \frac{dM}{dt} = \underline{M} = -m_e \sum_{k=2}^r Z_k n_k \bar{V}_k \Big|_{\text{neg. electrode}} = m_e \sum_{k=r+1}^{N-1} Z_k n_k \bar{V}_k \Big|_{\text{pos. electrode}} + m_e n_N \bar{V}_N \Big|_{\text{pos. electrode}} \quad (16)$$

or if each ion carries unit charge;

$$\underline{M} = m_e n_1 \bar{v}_1 \left|_{\substack{\text{neg} \\ \text{electrode}}} = m_e \left[n_N \bar{v}_N - n_1 \bar{v}_1 \right]_{\substack{\text{positive} \\ \text{electrode}}}$$

Either of these two equations shows that the constant mass flux, \underline{M} , is first order in m_e and therefore \underline{v}_0 is of order (m_e/m_1) . A good approximation then is to replace the set of equations, eq. 10, and eq. 11, by the set;

$$\underline{j}_i^0 = (n^2 e_i / \xi) \sum_{j=1}^N m_j D_j \underline{d}_j ; \quad i = 2, \dots, N$$

and

$$m_1 n_1 \bar{v}_1^0 = - \sum_{i=2}^N m_i n_i \bar{v}_i^0$$

which were obtained from eqs. 10, 11, and 3 by dropping \underline{v}_0 from eq. 10, and eliminating eq. 11 in favor of eq. 3 with \underline{v}_0 set to zero. The superscripts were added to the above to indicate this approximation. Iteration on eqs. 18 and 19 is easily accomplished by insertion of eq. 19 into eq. 17 (for singly charged ions), then a re-estimation of the current densities eqs. 10 and 11, etc. The latter are then expressed as a series expansion in essentially powers of the ratio of electron to ion mass.

Considerable simplification of the generalized force terms, eq. 8,

may be obtained by use of the mechanical equilibrium expression, eq. 6, after dropping the left hand inertial term. The approximate current densities (or the general form, eq. 10) became:

$$\underline{j}_i^o = \frac{e_i n}{kT} \sum_{j=1}^N m_j D_{ij} \left\{ kT \text{grad}(n_j - \delta_{ji} n) - (e_j n_j - \delta_{j1} \rho) \underline{E} \right\} \quad (20)$$

The Kronecker δ_{ij} 's have been inserted into this formula in order that the mobilities, defined below, have the standard limiting form for small ion concentrations. We then define the mobility as the proportionality coefficient between the current densities and the local electric field;

$$\mu_i^o \equiv \frac{-n}{n_i \xi kT} \sum_{j=1}^N m_j D_{ij} (e_j n_j - \delta_{1j} \rho); \quad i = 2, \dots, N. \quad (21)$$

This formula is the appropriate generalization of the mobility concept to multicomponent, weakly ionized gas systems for the lowest order in the ratio of electron to ion masses. More general expressions may be obtained in this matter by the indicated iteration scheme.

The kinetic theory of gases gives a relationship between the

multicomponent diffusion coefficients, and the experimentally accessible binary diffusion coefficients, which, in the first approximation of the kinetic theory, is explicit. Let the matrix be defined:⁽³⁾

$$F_{ij} = (1 - \delta_{ij}) \frac{1}{f} \left[\frac{n_1}{D_{ij}} + \frac{m_j}{m_i} \sum_{k \neq i} \frac{n_k}{D_{ik}} \right] \quad (22)$$

where the script D_{ij} are the binary diffusion coefficients of component i in component j and vice versa. These quantities are symmetric in the indicies. Now the generalized multicomponent quantities are given in terms of the inverse to the F matrix;

$$m_j D_{ij} = F_{ij}^{-1} - F_{ii}^{-1} \equiv G_{ij} \quad (23)$$

Therefore, the evaluation of these two equations and substitution of the result into eq. 21 gives the mobilities in terms of the binary diffusion coefficients.

Let us consider a simple, three-component system as an illustration of the above arguments. Suppose that the system is weakly ionized and that we may neglect the interaction of the ion species among themselves. Thus we have a system of neutral, positive and negative charges moving under the influence of various external forces at a rate determined by the ion-neutral interaction. Since the binary diffusion coefficients depend inversely on the interaction

cross sections; zero for the latter means that the corresponding coefficient is infinite. We then define the following:

$$D_{23} = D_{32} = \infty \quad (\text{no ion-ion interaction})$$

$$D = D_{12}; \quad K = D_{12}/D_{13}; \quad \delta = m_3/m_1 \approx m_3/m_2$$

The mole fractions of the ions are approximately;

$$c_2 = n_2/n_1 \quad \text{and} \quad c_3 = n_3/n_1$$

The matrix F may be written;

$$F = \frac{n_1}{\xi D} \begin{pmatrix} 0 & 1 & K \\ (1+c_2) & 0 & \delta \\ K(c_3+1/\delta) & K/\delta & 0 \end{pmatrix} \quad (24)$$

and its inverse is easily computed to be;

$$F^{-1} = \frac{\xi D}{n_1 \left(\frac{K^2}{\delta} + K + \frac{K^2 c_2}{\delta} + K c_3 \delta \right)} \begin{pmatrix} -K & K^2/\delta & \delta \\ K(1+c_3) & -K^2(1/\delta + c_3) & K(1+c_2) \\ \frac{K}{\delta}(1+c_2) & K(1/\delta + c_3) & -(1+c_2) \end{pmatrix} \quad (25)$$

The matrix G is

$$G = \frac{\xi D}{n_1 \left(\frac{K^2}{\delta} + K + \frac{K^2 c_2}{\delta} + K c_3 \delta \right)} \begin{pmatrix} 0 & K(1+K/\delta) & K+\delta \\ K+\frac{K^2}{\delta} + K c_3 + K^2 c_2 & 0 & K+\frac{K^2}{\delta} + K c_2 + K^2 c_3 \\ 1+\frac{K}{\delta} + \frac{K}{\delta} c_2 + c_2 & \frac{K}{\delta} + K c_3 + c_2 + 1 & 0 \end{pmatrix} \quad (26)$$

If written to first order in the ion densities, this matrix becomes;

$$G_T = \frac{eD}{n_1} \begin{pmatrix} 0 & 1 & \delta/k \\ 1 & 0 & 1 \\ 1/k & 1/k & 0 \end{pmatrix} + \frac{eD}{n_1(1+k/\delta)} \begin{pmatrix} 0 & -(\frac{k}{\delta}c_2 + c_3\delta) & -\frac{\delta}{k}(\frac{k}{\delta}c_2 + c_3\delta) \\ k(c_3 - \frac{1}{\delta}c_2) & 0 & c_2(1-k/\delta) + c_3(k-\delta) \\ \frac{1}{k}(c_2 - c_3\delta) & \frac{1}{k}[(k-\delta)c_3 + c_2(1-\frac{k}{\delta})] & 0 \end{pmatrix} + \dots \quad (27)$$

By eq. 21, the mobilities are;

$$\mu_2^o = \frac{eD}{kT} \left[1 + c_2 + c_3 - \frac{(c_2 - c_3\delta)}{(1 + k/\delta)} (k/\delta - \frac{n_3}{n_2}) \right] \quad (28)$$

and

$$\mu_3^o = -\frac{eD}{kT} \left[1 + c_2 + c_3 - \frac{(c_2 - c_3\delta)}{(1 + k/\delta)} \left(\frac{k}{\delta} - \frac{n_2}{n_3} - 1 \right) \right] \quad (29)$$

correct to first order in the ion densities. The leading terms of these two mobility expressions are the usual definitions given in terms of the binary diffusion coefficients. The additional terms represent effects arising from non-zero space charge, mass and geometry effects. If the negative charge carriers are electrons, then the mobilities should be generalized by the iteration scheme mentioned earlier to ensure that all relevant orders of the electron to ion mass ratio are retained. For the special case that

$$\delta = k = 1 \quad \text{and} \quad \rho = 0$$

we find that

$$\mu_2 = -\mu_3$$

as would be expected. Note that the limits of μ_2 and μ_3 as n_2 and n_3 pass to zero are infinite. That is;

$$\lim_{n_2 \rightarrow 0} e_2 n_2 \mu_2^0 E = -\frac{e^2 D}{kT} \frac{\delta}{1 + k/\delta} \frac{n_3^2}{n_1} E \Big|_{n_2=0} \text{ (pos. plate)} \quad (30)$$

and

$$\lim_{n_3 \rightarrow 0} e_3 n_3 \mu_3^0 E = \frac{e^2 D}{\delta kT} \frac{1}{1 + k/\delta} \frac{n_2^2}{n_1} E \Big|_{n_3=0} \text{ (neg. plate)} \quad (31)$$

These two expressions represent back currents flowing against the proper direction in the applied field. This is a result of the ion density gradients as shown by the equation of motion. If n_1 is assumed constant, we have;

$$\lim_{n_2 \rightarrow 0} e_2 \mu_2^0 n_2 E = \frac{e D \delta}{1 + k/\delta} c_3 \text{ grad } n_3 \quad (32)$$

and

$$\lim_{n_3 \rightarrow 0} e_3 n_3 \mu_3^0 E = \frac{-e D}{\delta kT} \frac{1}{1 + k/\delta} c_3 \text{ grad } n_2 \quad (33)$$

where the electric field has been replaced by the gradients of the

ion densities. The existence of these limits shows that the mobilities are not uniquely defined independent of the so-called "non-conductive" portion of the ion current densities, except to zero order in the ion concentrations. Eqs. 28 and 29 also show that the commonly employed experimental assumption⁽⁴⁾ that the ratio of mobility to the diffusion coefficient is a function only of the state of the gas is true only in regions of near zero space charge. Then the mobility exists and;

$$\frac{D}{\mu_2^0} = \frac{kT}{e} \left\{ 1 - c_2 - c_3 + \frac{(c_2 - c_3 \delta)}{(1 + \kappa/\delta)} \left(\frac{k}{\delta} - \frac{n_3}{n_2} \right) + \dots \right\}; n_3 \sim n_2 (n_2 \neq 0)$$

(34)

is a valid expansion of the ratio in the ion mole fractions.

This analysis gives a systematic correct procedure for the expansion of the general current densities, eq. 20, in a double series of concentration ratios and the ratio of electron to ion masses. Such expansions are required in order to systematically explore the shape of the ion density profiles near the electrodes of a closed conducting system.

Space Charge Effects in a Simple System

An interesting aspect of current conduction in weakly ionized systems is the modification of the various ion densities from point to point in the volume between the electrodes arising from a local space charge. Such effects have been dealt with extensively in the theory of thermionic devices, semiconductors, and magnetohydrodynamic systems, but not often in radiation counter design, or in analysis of certain conduction experiments. A study of devices in the last two categories prompted the considerations of this section.

A correct analysis of the ion densities near the electrodes to any given order in the densities would be based upon the analysis of the previous paragraphs. These polarization effects also are strongly influenced by any chemical reactions among the ions tending to modify the net fluid conductivity. In order to concentrate on this feature in a simple manner, it is fortunately possible to neglect the considerations of the previous section; that is neglect all gradients in the current densities, and assume constant mobilities, and still have a viable problem. Such a crude assumption violates the equation of mechanical equilibrium, eq. 6, which is particularly important near the electrodes, but nevertheless, sheath formation can still be represented in a semiquantitative way.

Let us consider a simple four component system consisting of neutral molecules, singly charged negative and positive ions, and

electrons. Further, the gas will be considered "weakly ionized" as described earlier. Suppose, then, that ionizing radiation falls uniformly on a gas system between plane parallel electrodes of diameter B meters and spaced d meters apart. The neutral component weakly ionizes into positive ions and electrons. The latter, in turn, are depleted by attachment to neutrals, forming negative ions, as well as being discharged at the positive electrode. Under steady state conditions, and a constant external voltage source, the ion populations are determined by two parameters proportional to the rate of ionization and the electron attachment frequency. If the ion-ion and ion-electron binary diffusion coefficients are set to infinity, the analysis of the preceding sections shows that the mobilities are proportional to the ion-neutral and electron-neutral binary diffusion coefficients. In MKS units, the positive and negative ion mobilities approximately the same and close to $.1 \text{ m}^2/\text{sec-volt}$ for most common gases at room temperature. The electron mobility under the same conditions is approximately a thousand times larger. Let μ be the ion mobility and μ_e be the correspondent electron number.[†] The rate of ionization in number of ions produced per cubic meter per second is N , the applied voltage V_0 , and the attachment frequency is ν . Let n^+ , n^- and n_e represent the ion and electron densities. Dimensionless densities for each of these species are easily defined;

$$\eta^+ = \frac{n^+ \mu E_o}{Nd} \quad ; \quad E_o \text{ is the applied field} \quad (35)$$

$$\eta^- = \frac{n^- \mu E_o}{Nd} \quad (36)$$

and

$$\eta_e = n_e \mu_e E_o / Nd \quad (37)$$

A dimensionless ionization rate and an attachment frequency may be formed:

$$A = e d^2 N / E_o^2 \epsilon_o \mu \quad (38)$$

$$\gamma = \nu d / \mu_e E_o \quad (39)$$

Typical values for these two parameters are, $A = 1.8$, and $\gamma = .1$ for $d = 10^{-3}$, $N = 10^{22}$, $E_o = 10^5$, and $\nu = 10^8$ with the mobilities as given. Let $z = x/d$ be a dimensionless length, then the continuity equations and the electric field equation are;

$$-\frac{d}{dz} (\eta_e \mathcal{E}) = 1 - \gamma \eta_e \quad ; \quad \mathcal{E} = E/E_o \quad (40a)$$

$$-\frac{d}{dz} (\eta^- \mathcal{E}) = \gamma \eta_e \quad (40b)$$

$$+ \frac{d}{dz} (\eta + \mathcal{E}) = 1 \quad (40c)$$

and

$$\frac{1}{A} \frac{d}{dz} \mathcal{E} = \eta^+ - \eta^- - \frac{\mu}{\mu_e} \eta_e \quad (41)$$

The boundary conditions on these equations are that the various ion densities vanish at the electrodes of the same sign. The sum of eqs. 40a and 40b, and eq. 40c permit trivial quadrature. With the given boundary conditions, we find that;

$$(\eta_e + \eta^-) \mathcal{E} = (1 - z) \quad (42a)$$

and

$$\eta^+ \mathcal{E} = z \quad (42b)$$

which may be combined with the field equation, eq. 41 to produce the result after differentiation;

$$\frac{1}{A} \frac{d^2}{dz^2} \left(\frac{1}{2} \mathcal{E}^2 \right) = \gamma \eta_e + 1; \left(\frac{\mu}{\mu_e} \sim 0 \right) \quad (43)$$

Then multiplication by \mathcal{E} , differentiation, and substitution from eqs. 40a and eq. 43, followed by a simple quadrature, we arrive at the final electric field equation;

$$\epsilon^2 \epsilon'' = \epsilon(A - \epsilon'^2 - \gamma \epsilon') + A \gamma (2\gamma - 1) ; \gamma = z - 1 \quad (44)$$

where the boundary condition,

$$\epsilon \epsilon' = A @ \gamma = 0 \quad (45)$$

has been used to evaluate the constant of integration. Eq. 45 and the additional boundary condition that the average electric field be equal to the applied field,

$$\int_0^1 \epsilon(\gamma) d\gamma - 1 = 0$$

completes the specification of the solutions to eq. 44. This equation must be handled numerically in all but the simplest of systems, and has been treated thus in this paper. Once the electric field and its first derivative has been found, the ion densities follow from eqs. 42a, 42b, and 41. The results of the Runge-Kutta numerical integration of eq. 44 are shown in figs. 1-9. These plots represent the schematic cross section of a cell with the negative plate, viewed edgewise, at the left along the relative magnitude scale. The positive electrode, similarly viewed, is placed at 1 on the distance scale along the abscissa. Each figure in this sequence shows the spacial distribution of the three charged species and the actual electric field. The horizontal line at 1 on the vertical axis represents the applied field. Figures 1 through 5 show the variation of the ion

distributions and the electric field for fixed ionization rate as a function of the electron attachment parameter γ , as it varies from 0 to 10 in several steps. The ion sheath regions near the electrodes in these figures may be identified by the positive departure of the actual electric field from the applied (horizontal line) field. The large free electron population that exists for small values of the electron attachment coefficient, destroys the symmetry of the sheaths in the first three figures. Here we see a very pronounced sheath at the negative electrode and none at the positive one. The more symmetrical patterns in \mathcal{E} for γ in excess of 5 show sheath formation at both electrodes. Figs. 6 and 7 show ion, electron and field distributions at half the dose rate of ionization than in the previous series. As expected, the electric field shows less deviation from the applied value, and a variation of the electron attachment frequency between 1 and 50 shows a relatively minor adjustment of the center of charge distribution. On the other hand, the series of figures, 2, 6, 8, and 9, shows a pronounced development of sheaths as the dose rate is quadrupled. Even though there is some question about the stability of the Runge-Kutta integration procedure in the case of fig. 9, qualitatively we see that the sheath regions dominate the volume, and that the local electric field is nearly zero at one point. The ions are "trapped" in this region of small field, and if ion-ion recombination is permitted, will appreciably affect the total current drawn, even

though the average ion density would be such as to neglect this mechanism.

Fig. 10, based upon the relation between the ion current densities and the external current shown in Appendix A, gives the ratio of the electron to the negative ion current for this model as a function of the electron attachment frequency. A family of such curves exist for each value of the ionization rate, A , and E_0/p . The uniqueness of these functions suggests an experiment wherein the electron attachment is measured as a function of the latter two quantities. This may be accomplished by simultaneously determining the free electron population in a cell and measuring the external current flow in a gas with prominent electron attachment such as oxygen. Hence possible concentration effects in the attachment frequency of this or a similar gas interpreted by the previous section's analysis, may be sought for.

Conclusions

This paper has considered several complementary aspects of current conduction in weakly ionized, multicomponent gases. The first of these is the systematic generalization of the ion current densities under steady state conditions in terms of the kinetic theory multicomponent diffusion coefficients. From this follows an expansion of the current densities in essentially the ion concentrations,

and the known binary diffusion coefficients. The usual definition of ion mobility also shows an ion concentration dependence and a lack of uniqueness near the system electrodes if first order terms in the ion concentrations are retained. The often quoted result that the ratio of the binary diffusion coefficient to the ion mobility is a function only of temperature is shown to be valid only in regions of negligible space charge and then in the limit of zero ion concentrations. (This result follows by generalization of the two ionized component example given in the first section.)

The second section of this paper deals with an example of space charge effects in a simple, chemically reactive system. Here the ion densities and the local electric field were numerically calculated as a function of the ionization intensity and the electron attachment frequency. The results show sheath formation at the electrodes under these various conditions even though the analysis is quantitatively inaccurate by the considerations of the first section. A plot of the ratio of electron to negative ion current conducted in the external circuit as a function of the electron attachment frequency provides a possible basis of determination of the latter under various ionization conditions and ratio of E_0/p ; the applied electric field to the pressure.

Appendix A

At every point in the vessel between the electrodes, the electric field influencing the motion of the ions is the sum of the applied and space charge fields. In the absence of magnetic fields, the space charge field may be written as the gradient of a potential. Therefore,

$$\underline{E}_s = -\text{grad } \phi_s \quad (\text{A1})$$

and thus Poisson's equation is;

$$-\text{divgrad } \phi_s = \rho / \epsilon_0 \quad (\text{A2})$$

We assume the boundary conditions;

$$\phi_s = 0 \quad (\text{A3})$$

on the electrode surfaces.

In a similar way, the applied field is also the gradient of a potential;

$$\underline{E}_0 = -\text{grad } V \quad (\text{A4})$$

where now V is the solution to Laplace's equation,

$$\text{div grad } V = 0 \quad (\text{A5})$$

with the boundary conditions,

$$V = V_0 \text{ positive electrode, and } V = 0, \text{ negative electrode} \quad (\text{A6})$$

A consideration of Maxwell's equations establishes the relation between the total current density in the system and the external current. The scalar product of the first Maxwell's equation with \underline{E} ;

$$\underline{E} \cdot \text{curl } \underline{H} = \left[\underline{j} + \epsilon_0 \frac{\partial \underline{E}}{\partial t} \right] \cdot \underline{E} \quad (\text{A7})$$

and the second with \underline{H} ;

$$\underline{H} \cdot \text{curl } \underline{E} = -\mu_0 \left(\frac{\partial}{\partial t} \underline{H} \right) \cdot \underline{H} \quad (\text{A8})$$

when summed together may be written;

$$-\text{div } (\underline{E} \times \underline{H}) = \underline{j} \cdot (\underline{E}_0 + \underline{E}_s) + \frac{\partial}{\partial t} \left[1/2 \epsilon_0 (\underline{E}_0 + \underline{E}_s)^2 + 1/2 \mu_0 H^2 \right] \quad (\text{A9})$$

with the aid of the well-known vector identity;

$$-\text{div } (\underline{E} \times \underline{H}) = \underline{E} \cdot \text{curl } \underline{H} - \underline{H} \cdot \text{curl } \underline{E} \quad (\text{A10})$$

On the other hand, if S represents the surface of the volume, the integral, $\int_S (\underline{E} \times \underline{H}) \cdot d\underline{s}$ is the flux of power through the surface, which, in the absence of electromagnetic radiation, is just $-IV_o$, where I is the external circuit current. After dropping the magnetic field term, the power expression above becomes;

$$IV_o = \int_V d\underline{r} \cdot \underline{j} \cdot (\underline{E}_o + \underline{E}_s) + \int_V d\underline{r} \cdot \frac{\partial}{\partial t} \left[\frac{1}{2} \epsilon_o (\underline{E}_o + \underline{E}_s)^2 \right] \quad (A11)$$

If we assume the geometry of the active volume is such that the non-electrode walls parallel the applied electric field lines, then the cross term in the applied and space charge fields may be shown to vanish by means of the boundary conditions on ϕ_s . Also, from eq. A2 and conservation of charge, we find that;

$$\frac{1}{2} \epsilon_o \frac{\partial}{\partial t} E_s^2 = -\text{div} \left[\epsilon_o \phi_s \frac{\partial E_s}{\partial t} + \phi_s \underline{j} \right] - (\underline{j} \cdot \underline{E}_s) \quad (A12)$$

Where again the surface integral vanishes by the boundary conditions on ϕ_s . Thus we are left with the final, simple formula;

$$IV_o = \int_V d\underline{r} (\underline{j} \cdot \underline{E}_o) + \frac{1}{2} \epsilon_o \frac{\partial}{\partial t} \int_V d\underline{r} E_o^2 \quad (A13)$$

For steady, applied potentials, the last term on the right-hand side vanishes. If a circuit has an external load resistance R and a voltage source V' across both resistor and cell, we find the following implicit equation for the external current;

$$I = \frac{V'}{2R} \left[1 - \left\{ 1 - \frac{4R}{V'^2} \int_V d\mathbf{r} \cdot (\underline{j} \cdot \underline{\tilde{E}}(I)) \right\}^{\frac{1}{2}} \right] \quad (A14)$$

where $\underline{\tilde{E}}(I)$ means that the boundary condition, A6, must be replaced by

$$\tilde{V} \Big|_{\substack{\text{pos.} \\ \text{electrode}}} = V' - IR \quad (A15)$$

Footnotes

† We should make clear at the outset that we are not considering sheath formation at walls and electrodes of the cell in the usual plasma sense. Our concern is with the macroscopic charge imbalance established by the current flow fields and the boundary conditions at the electrodes. A measure of the effect of ion-ion interactions in modifying the Coulomb potential is the Debye length, ;

$$\lambda_D = \left(\frac{\epsilon_0 \kappa kT}{n_i e^2} \right)^{\frac{1}{2}}$$

where κ is the specific inductive capacity of the medium and n_i is an ion density. If we are to ignore ion-ion interactions, then either

$$\lambda_D \gtrsim d \quad (\text{weak ionization})$$

where d is some relevant dimension of the cell, or;

$$\lambda_D \gtrsim \lambda_f \equiv \left(\frac{nkT}{\rho E} \right)_{\text{electrode}} \approx \left(\frac{n_1}{n_i} \right) \left(\frac{kT}{e} \right) \frac{1}{E}$$

The new length, λ_f is a scale of the ion gradient set up against the influence of thermal agitation by the applied field at the electrodes. For the conditions considered in the problem in this paper, the weak ionization approximation holds; for

$$n_e \leq 10^6 \text{ cm}^{-3}$$

Ionized gases with ion densities of the order of 10^{12} cm^{-3} satisfy the second inequality if the other parameters are the same as those discussed in the paper.

‡ A constant electronic mobility is a very crude approximation. In practice, an empirical curve - fit of the electron mobility in the specific gas studied is required over the desired range of E/p .

Bibliography

- 1) P. M. Livingston, J. Appl. Phys., 35, pp. 2341-2348 (1964).
- 2) S. R. DeGroot and P. Mazur, Non-equilibrium Thermodynamics, (North-Holland Publishing Co. Amsterdam, 1962).
- 3) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, (John Wiley and Sons, New York, 1954).
- 4) e.g., L. M. Chanin, A.V. Phelps, and M. A. Biondi, Phys. Rev. 128, pp. 219-230, (1962).

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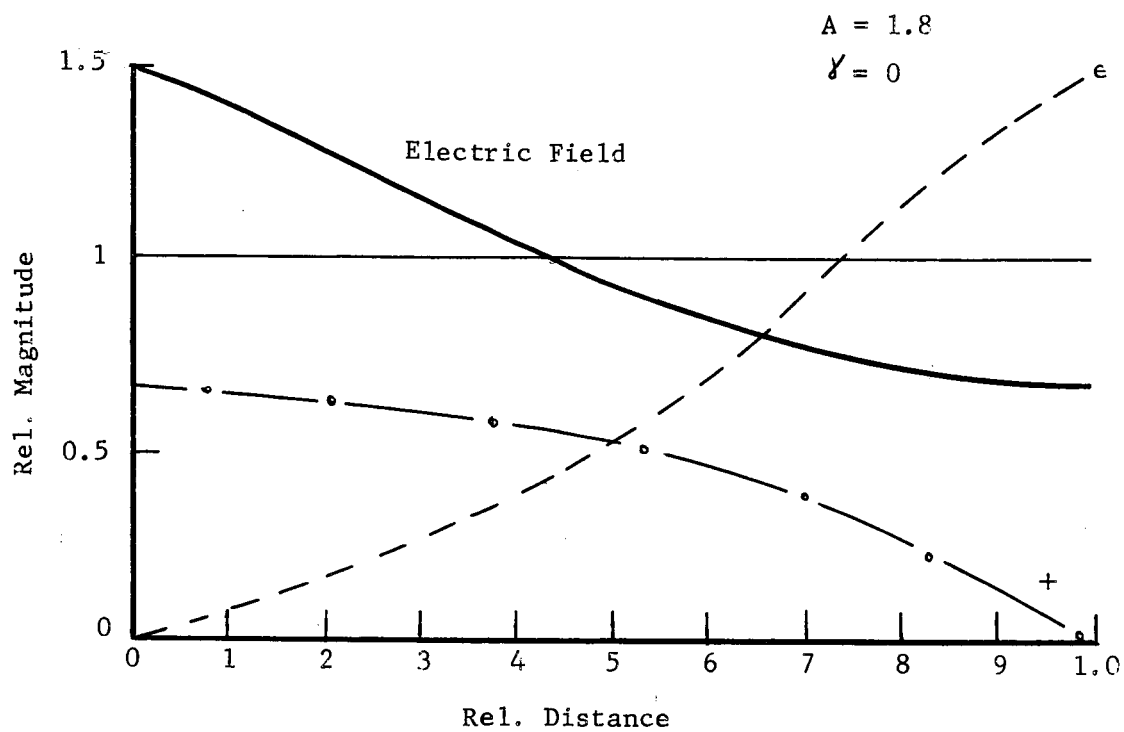


Fig. 1

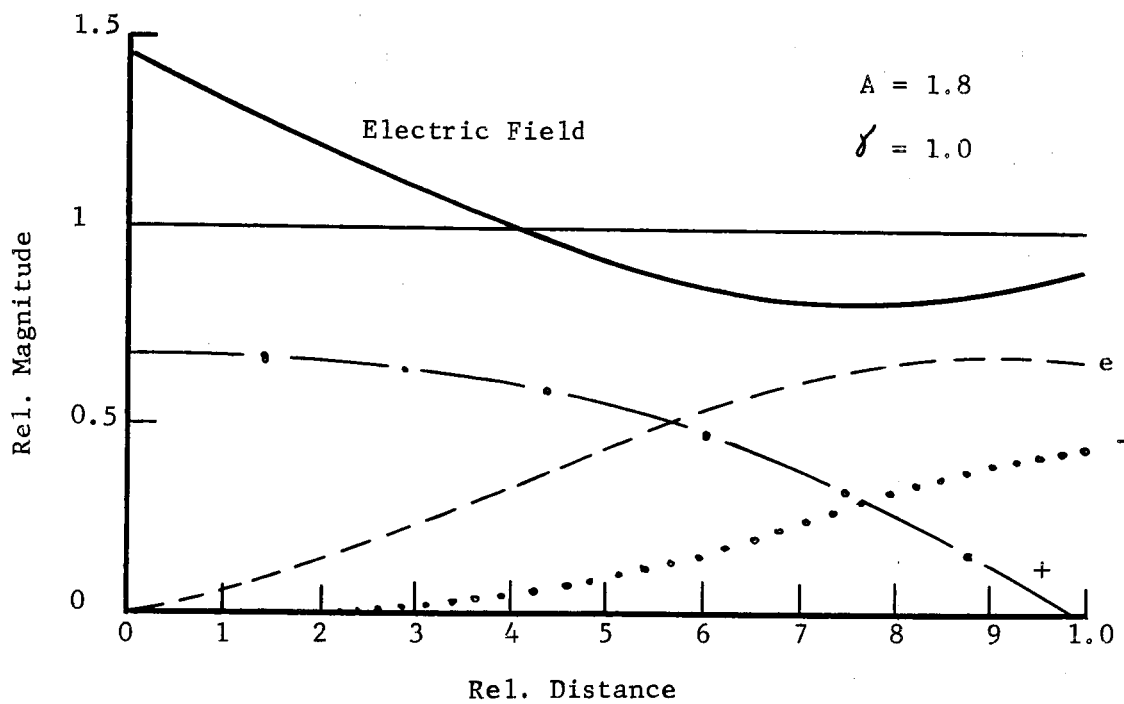


Fig. 2

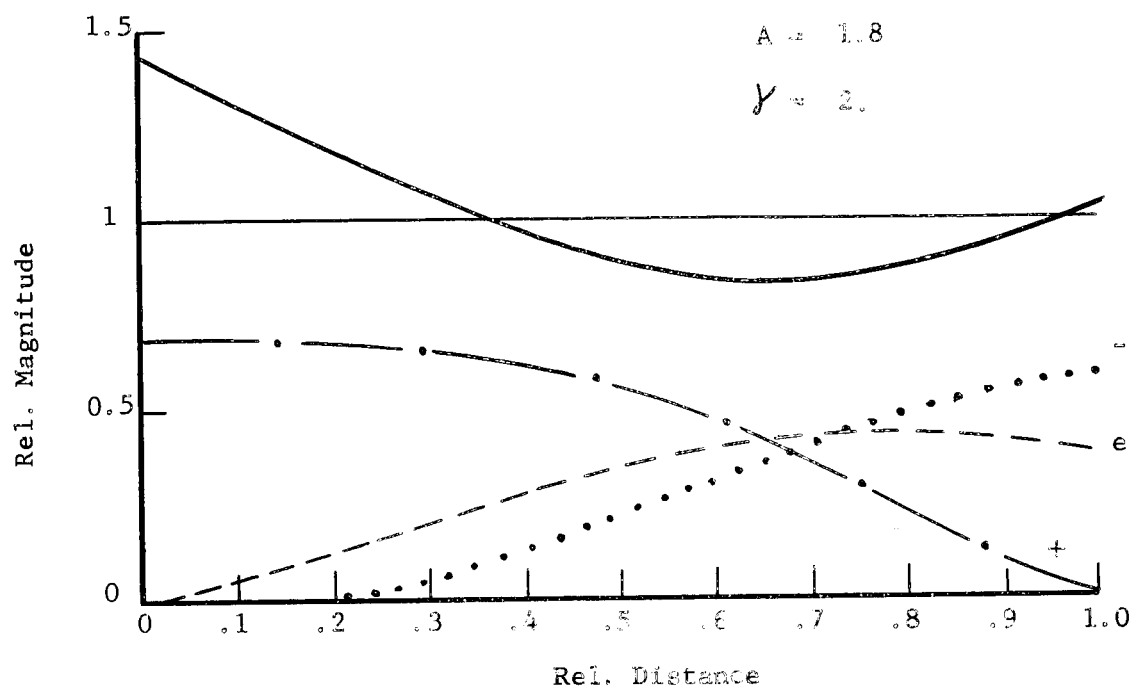


Fig. 3

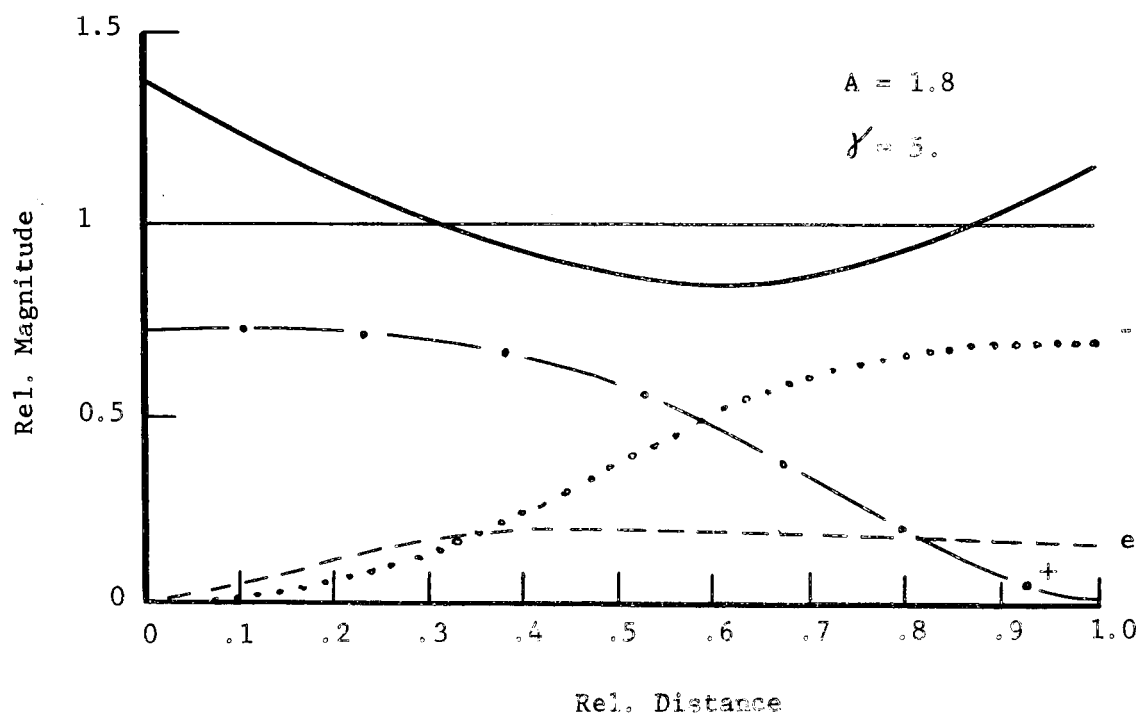
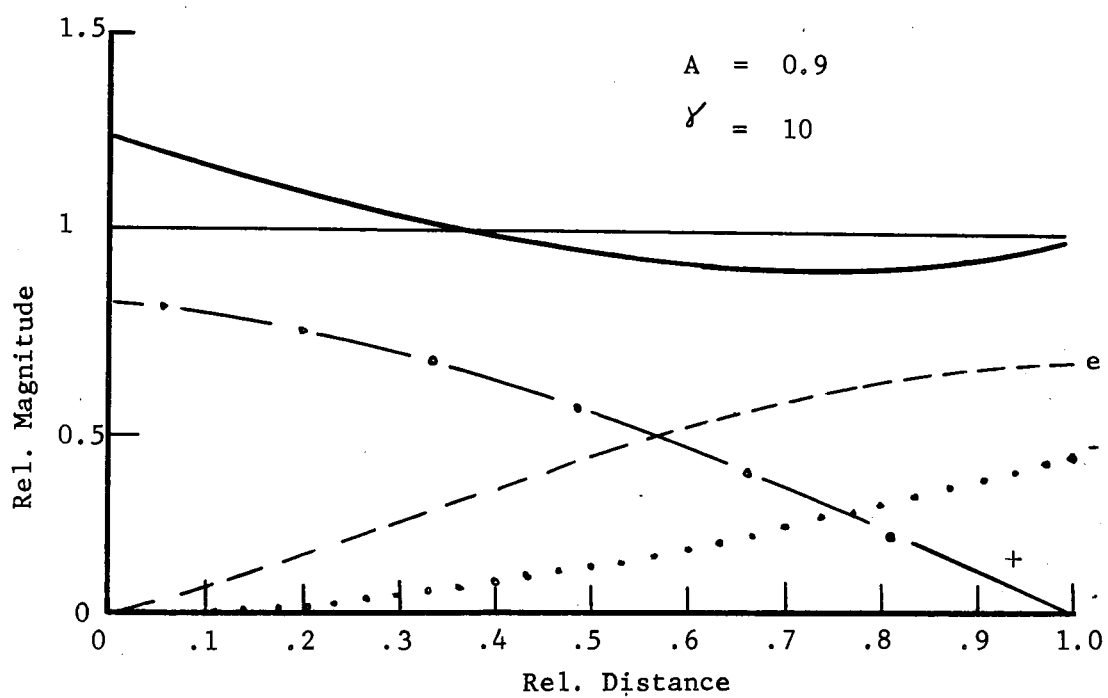
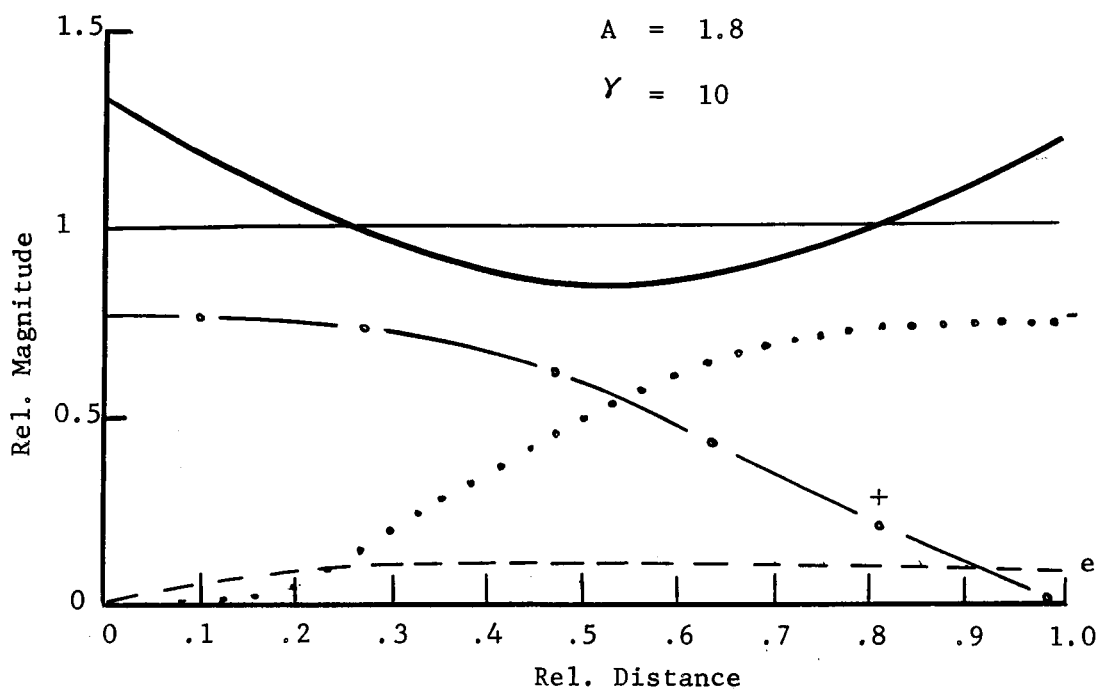


Fig. 4



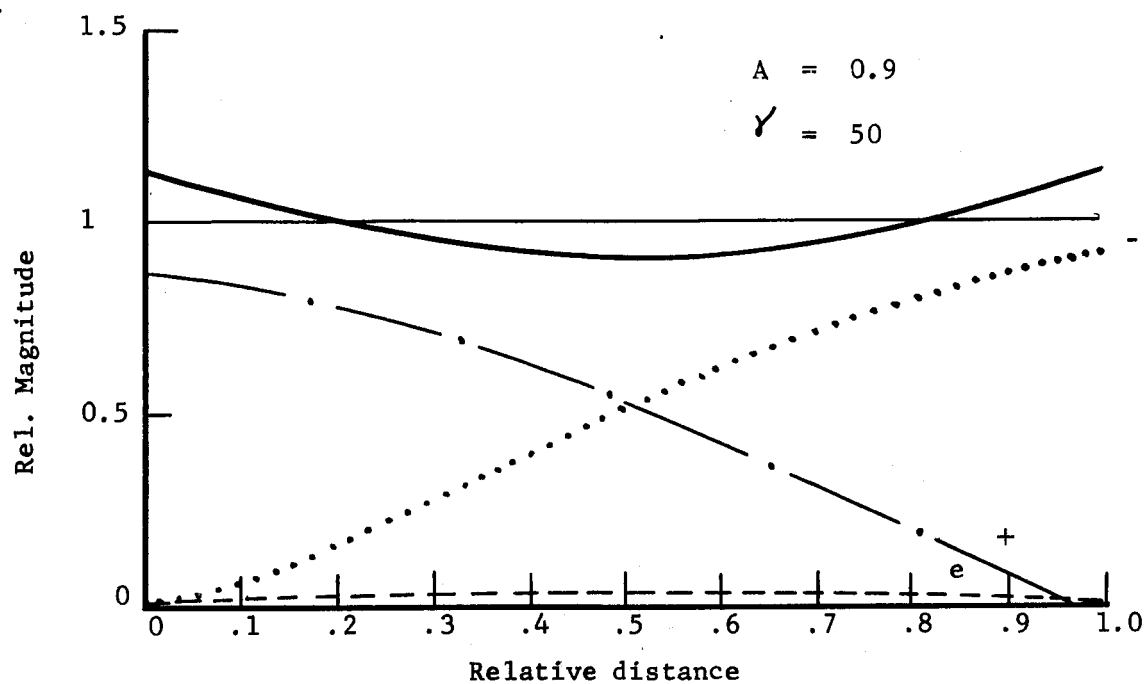


Fig. 7

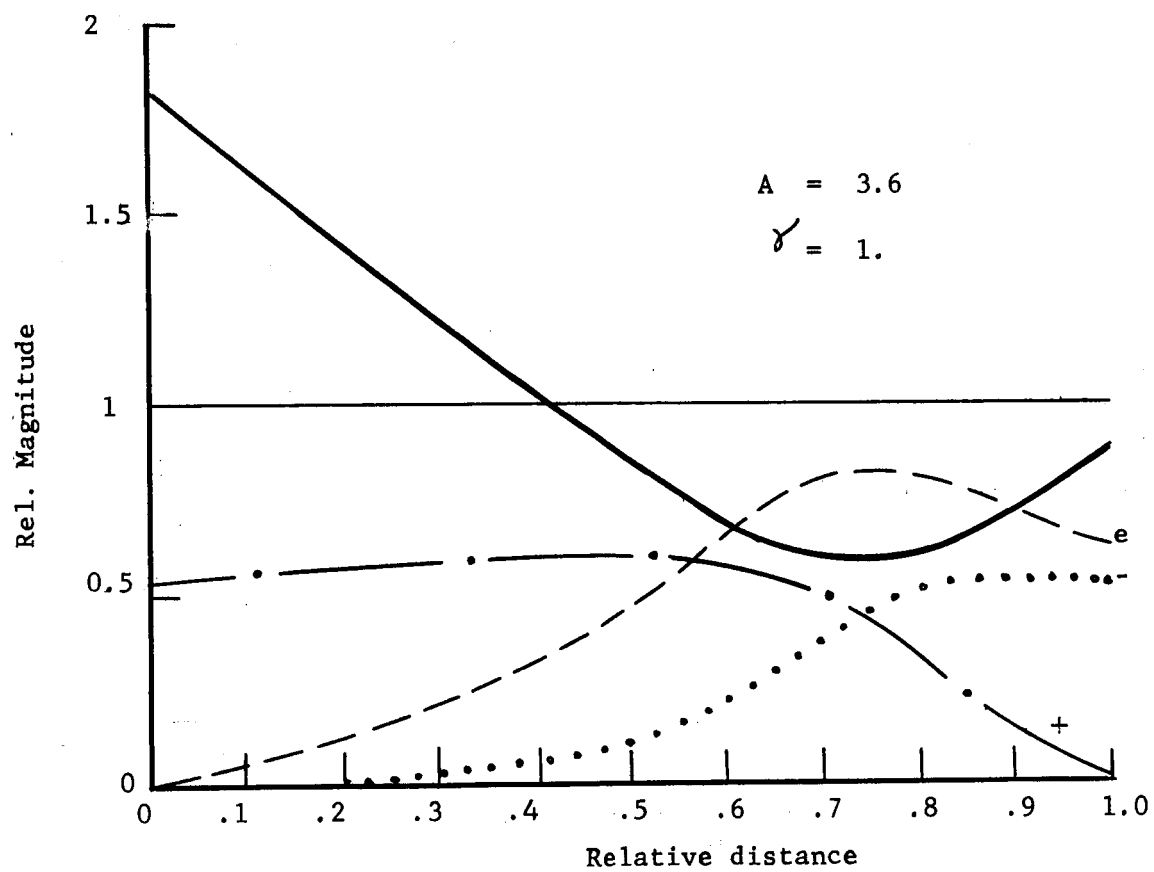
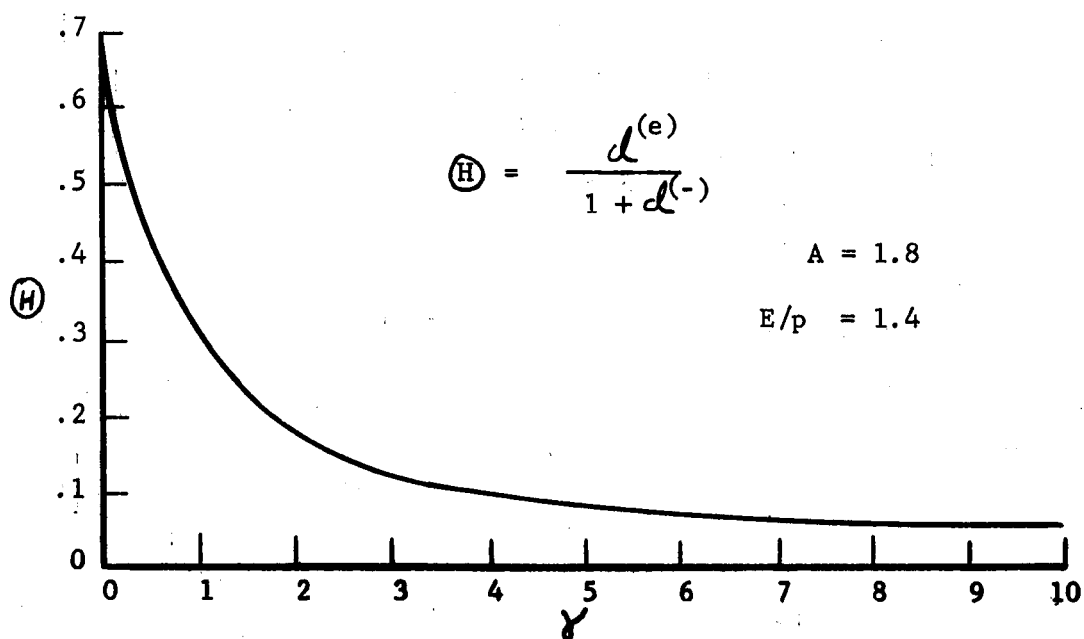


Fig. 8



The Dimensionless Attachment Frequency as a Function of H

Fig. 9

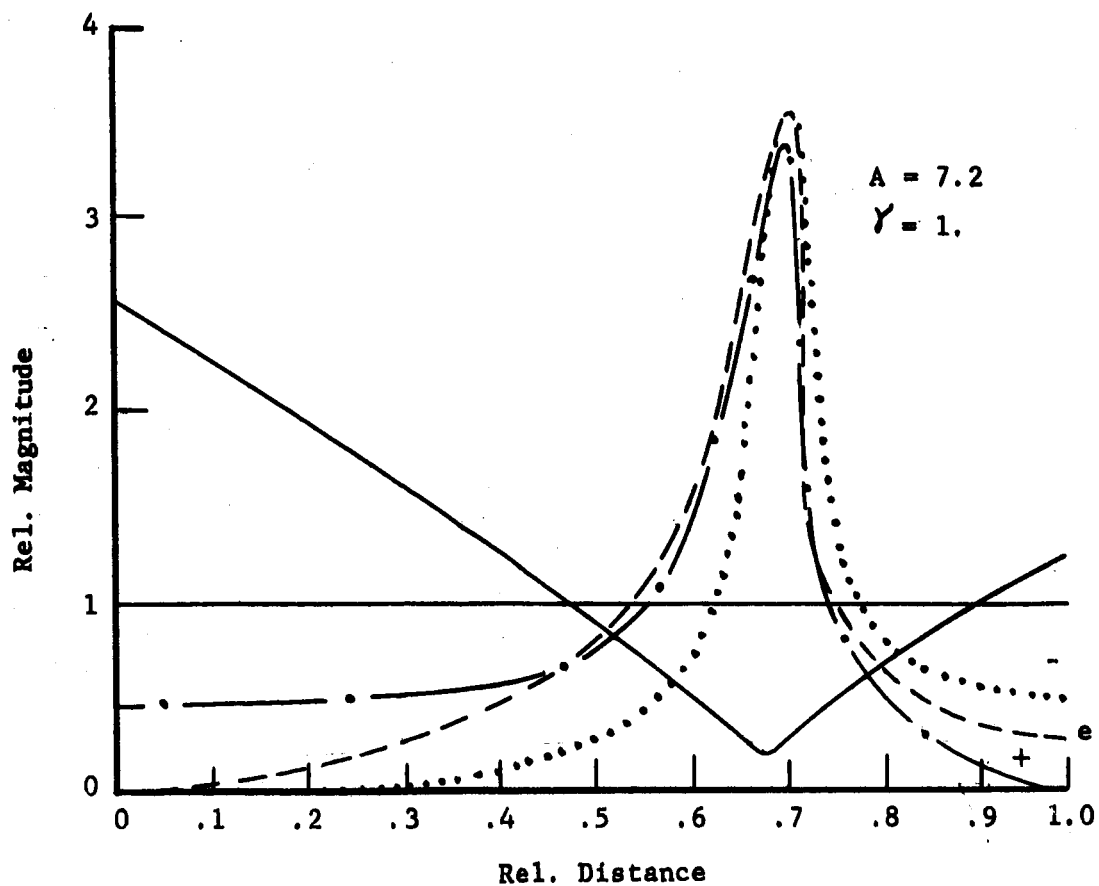


Fig. 10